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(54) **Syringe needle**

(57) Provided is a syringe needle with its piercing resistance lowered, its resistance not increased even when piercing is repeated and the sterilizing means not limited.

A syringe needle coated on its outside a mixture of a first polyorganosiloxane resulting from reaction of an alkoxysilane containing epoxy group and both terminal amino groups, and a second non-reactive polyorganosiloxane which the mean degree of polymerization of siloxane part is less than that of the first polyorganosiloxane.

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**Description****[DETAILED DESCRIPTION OF THE INVENTION]**5 **[INDUSTRIAL FIELD OF APPLICATION]**

The present invention relates to a syringe needle with its surface coated with polyorganosiloxane.

**[PRIOR ART]**

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An art of treating the metal surface with a silicone compound for lowering the surface resistance has hitherto been practiced. In Pat. Pub. Sho 46-3627, for example, laid open is a metal cutting blade having in its surface an adhesive layer with siloxane units having amino groups and organosiloxane units. When this layer of adhesive coating is applied to syringe, the problem of adhesive coating substance being separated when injection attempt is repeated. Such repeated attempts to inject are done when a drug solution is introduced into a syringe tube with its needle penetrated through the rubber stopper of vial bottle and having it introduced into the human body after letting the liquid medicine into syringe cylinder. Another product was that since the invention was bound to increase the piercing resistance due to gamma ray resistance, hence an effective sterilizing method had to be found other than gamma ray irradiation.

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Meanwhile, in Pat. Pub. Sho 61-35870 introduced is a syringe needle excelled in piercing properties by causing to have it reacted with polydiorganocyclohexane having terminal silanol groups and then hardening it at the room temperature or by heating at 100~150°C. Since the coating agent applied to the syringe needle was mixed with an epoxy group-containing silane and hence was excelled in hardening property, the piercing resistance was not sufficiently lowered and pain to the patient could not be lowered.

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Further, according to Pat. Laid-open Hei 7-178159, introduced is a syringe needle coated with a coating agent comprising a specific amino group-containing polyorganosiloxane and specific polyorganosiloxane, and surface-treated by a curing method by, among others, by a hardening method including gamma-ray irradiation. Although in the present invention the resistance to syringe needle piercing is lowered by curing the coating agent, the resistance to piercing is not necessarily low, and problematic was that the sterilization method was limited to gamma-ray irradiation.

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30 **[PROBLEM TO BE SOLVED BY THE INVENTION]**

The present invention is for solving the aforementioned problem and is aimed at providing a syringe needle with the resistance to piercing is lowered, the resistance is not increased even when piercing is repeated and is aimed at provision of piercing needle with no limitation to sterilizing means.

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**[MEANS FOR SOLUTION OF PROBLEMS]**

After intensive research for solving such conventional defects the present inventors et al. discovered that the aforementioned problem could be solved by coating the syringe needle with a mixture of polyorganosiloxane resulting from a mixture of polyorganosiloxane resulting from reaction of epoxy group-containing alkoxysilane with terminal amino groups and arrived at the present invention.

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That is, the present invention relates to a syringe needle coated on its outside a mixture of a first polyorganosiloxane resulting from reaction of an alkoxysilane containing epoxy group and both terminal amino groups, and a second non-reactive polyorganosiloxane which the mean degree of polymerization of siloxane part is less than that of the first polyorganosiloxane.

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It is preferred that the mean degree of polymerization of the first polyorganosiloxane resulting from reaction of epoxy group-containing alkoxysilane terminal amino groups at both ends is 10~10,000. Also preferred is that the quantity of the second non-reactive polyorganosiloxane is 1/10 ~ 7/10 of polyorganosiloxane in weigh ratio.

50 **[FORM OF EMBODYING THE INVENTION]**

The first polyorganosiloxane with epoxy group-containing alkoxysilane reacted to terminal amino-groups is synthesized by the use of polyorganosiloxane having silanol groups at both terminals. That is, reaction is carried out in two stages in a solvent as follows. In the first stage amino group-containing alkoxysilane is caused to react on polyorganosiloxane having silanol groups at both terminals. In the second stage the reaction product in silanol group is caused to react with alkoxysilyl-group containing alkoxy-silyl group. In the reaction in the second stage amino group of amino group of amino group-containing alkoxysilane oxythe is caused to react with epoxy group of epoxy group-containing alkoxysilane. In the reaction in the first stage silanol group reacts with alkoxysilyl group of amino group-containing alkox-

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ysilane. In the reaction in the second stage mainly amino group of amino group-containing alkoxy silane reacts with epoxy group of epoxy group-containing alkoxy silane. The first polyorganosiloxane thus obtained has at its both terminals amino group and alkoxy silyl group. As amino group-containing alkoxy silane may be cited N- $\beta$ -(aminoethyl) $\gamma$ -aminopropylmethyldimethoxysilane, N- $\beta$ -(aminoethyl) $\gamma$ -aminopropyltriethoxysilane,  $\gamma$ -aminopropylmethoxysilane,  $\gamma$ -aminopropylmethyldiethoxysilane,  $\gamma$ -aminopropyltriethoxysilane etc. As epoxy group-containing alkoxy silane may be coated  $\gamma$ -glycidoxypropyltrimethoxysilane,  $\gamma$ -glycidoxypropylmethyldiethoxysilane,  $\gamma$ -glycidoxypropyltriethoxysilane,  $\beta$ -(3,4-epoxy-cyclohexyl) ethyltrimethoxysilane and the like.

In the aforementioned reaction amino group-containing alkoxy silane may be reacted with epoxy group-containing alkoxy silane in the first stage and this reaction product may be reacted with polyorganosiloxane having silanol groups at both terminals in the second stage. In this case, in the first stage amino groups amino of amino group-containing alkoxy and epoxy groups of epoxy group-containing alkoxy silane are reacted. In the second stage of reaction alkoxy silane as the reaction product reacts with terminal silanol groups having terminal silanol groups. Anyway, the wanted composition is obtained by a known means.

The resulting composition may be mixed with the second non-reactive polyorganosiloxane and be diluted with a solvent to a nonvolatile concentration of about 5%. The mean degree of polymerization of the siloxane part of the second non-reactive polyorganosiloxane is less than the mean degree of polymerization of the siloxane part of the first polyorganosiloxane resulting from reaction of epoxy-containing alkoxy silane to amino groups at both terminals. If the mean degree of polymerization of the second non-reactive polyorganosiloxane is higher, the progress of cross-linking reaction of polyorganosiloxane having caused reaction of epoxy group-containing alkoxy silane to amino groups are both terminals with simultaneous failure of formation of good cross-linking units and the resulting syringe needle is high in piercing resistance and is inferior in piercing properties when piercing attempt is repeated.

A syringe needle of the present invention is dipped is obtainable by repeatedly dipping the needle and allowing the same thereafter. When left at the room temperature alkoxy silyl groups are formed on its surface by condensation reaction and the alkoxy silyl-type of layer may thus be formed. This kind of reaction may be enhanced by addition of proper organic acid such as acetic acid and for enhancing the reaction the reaction temperature may be raised to 100°C or the time of heating may be extended as necessary. When left the room temperature, the syringe needle has deposited thereon a layer of alkoxy groups to form a cross-linking film. For enhancing the reaction an organic acid such as acetic acid may be added or heating may be continued for some 1 hour at 100°C. Then, the second non-reactive polyorganosiloxane exists in the cross-linked unit regardless of such reaction to play a role of revealing lubricity. That is, a syringe needle is obtained covered with epoxy group-containing alkoxy silane reacted to the amino groups at both terminals. As syringe needle may be cited injection needles, winged needles, retained needles or the like with no particular limitation.

In a mixture of the first siloxane and the second non-reactive of polyorganosiloxane, the mean degree of polymerization of the siloxane part of the first polyorganosiloxane resulting from reaction of epoxy group-containing alkoxy silane when it is reacted to the terminal groups is preferred to be 10~10,000. If the polymerization degree of siloxane part is less than 10, cross-linking is difficult with the second non-reactive polyorganosiloxane mixed and there is an increased difficulty of favorable cross-linking unit being formed. Still more preferably it is in a range of 10~1,000. It is preferred that the ratio of the second non-reactive polyorganosiloxane to the first polyorganosiloxane is 1/10~7/10. If it is less than 1/10, resistance at the time of piercing tends to be increased, while, if it is less than 1/10, resistance at the time of piercing tends to be increased, while, if the syringe needle is inferior in repeated piercing behavior, it is in excess of 7/10.

The syringe needle covered with such cross-linking unit is not only less in resistance at the time of piercing and is safer from increase in piercing resistance for the piercing property is not lowered in the event of prolonged leaving and there is no risk of discoloration. Further, since it is a preferred cross-linking unit with a metal firmly bonded, there is no risk of a metal being solved into blood. The metal already hardened well, the resistance to gamma ray radiation does not result from continued hardening attempt and also contact with ethylene oxide gas is decreased rather than increasing (See Table 1.). Thus, the sterilizing method for the syringe needle of the present invention is not limited to radiation by syringe needle of the present invention.

Examples of the invention will be specified herein after.

#### [Example 1]

5 weight parts of silicone compound (MD x 4 — 4159, Dow Corning Inc., mean degree of polymerization: ca. 70) and 0.2 weight parts of  $\gamma$ -glycidoxypropyl methyldimethoxysilane (KBM-402, manufactured by Shin-etsu Chemical Co., Ltd.) were caused to react for 3 hours at 80°C. After completion of the reaction a colorless and transparent coating liquid was obtained with addition of 2.5 weight parts of polydimethyl siloxane (KF-96 50cSt, manufactured by Shin-etsu Chemical Co., Ltd., mean degree of polymerization:abt.50) and 82.3 weight parts of dichloropentafluoropentane (AK-225, manufactured by Asahi Glass Co., Ltd.). A 21G injection needle was dipped in this coating liquid and treatment was continued for 1 hour at 100°C.

The syringe needle thus obtained was let through a natural rubber sheet 1.5 mm in thickness, 30 in hardness at a

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crosshead speed of 100 mm/min. and the then resistance value was measured with universal tester AG-500 of Shimadzu Corp. The resistance when the edge has penetrated through the natural rubber sheet (first and fifth attempts) and the way silicone has reached the sheet surface are shown in Table 1.

### 5 [Example 2]

0.1 weight part of  $\gamma$ -aminopropyltriethoxysilane (KBE-903, manufactured by Shin'etsu Chemical Co., Ltd.) and 0.1 weight part of  $\gamma$ -glycidyloxy-propylmethyldimethoxysilane (KBM-402, manufactured by Shin'etsu Chemical Co., Ltd.) were caused to react for 3 hours at 80°C. This reaction product was added to a mixture of 3 weight parts of polydimethylsiloxane (mean degree of polymerization abt. 300) having cyanol groups at both ends and 10 weight parts of toluene and were caused to react for 12 hours at 80°C. After completion of reaction 3 weight parts of polydimethylsiloxane (DC-360 350 cSt, Dow Corning Corp., mean degree of polymerization abt. 200), 5 weight parts of n-decane and 78.8 weight parts of dichloropentafluoropropane were added to obtain a colorless, transparent coating solution. A 21G syringe needle was dipped in the coating liquid and heat-treated for 1 hour at 100°C. The syringe needle thus obtained was studied in the same way as in Example 1 and the result is shown in Table 1.

### [Example 3]

A 21G syringe needle was dipped in the coating liquid and sterilized with ethylene oxide gas instead of 1 hour heat treatment at 100°C. The syringe needle thus obtained was studied in the same way as in Example 1, and the result is shown in Table 1.

### [Example 4]

A 21G syringe needle was dipped in the coating liquid and sterilized by gamma ray irradiation instead of heating for 1 hour at 100°C. The syringe needle thus obtained was studied in the same way as in Example 1, and the result is shown in Table 1.

### [Comparative example 1]

Instead of polydimethylsiloxane used in polydimethylsiloxane used in example 1 polydimethylsiloxane having a viscosity of 12,500 cSt (DC-360 12,500 cSt, Dow Corning Inc., mean polymerization degree ca. 850) was used. The injection needle thus obtained was studied in the same way as in Example 1 and the result is shown in Table 1.

### 35 [Comparative example 2]

Instead of polydimethylsiloxane having a viscosity of 350 cSt polydimethylsiloxane having a viscosity of 12,500 cSt (DC-360 12500 cSt, Dow Corning Inc., mean degree of polymerization ca.850) was used, and the result is shown in Example 1.

|                | Piercing resistance (g) |          | Aherence of silicone |
|----------------|-------------------------|----------|----------------------|
|                | 1st time                | 5th time |                      |
| Example 1      | 11.3                    | 11.5     | Minor                |
| Example 2      | 9.1                     | 9.7      | Very minor           |
| Example 3      | 8.5                     | 9.2      | Very minor           |
| Example 4      | 9.3                     | 9.5      | Very minor           |
| Comp.example 1 | 14.7                    | 23.5     | Very major           |
| Comp.example 2 | 11.5                    | 17.3     | major                |

As is apparent from the result shown in Table 1, the syringe needle referred to in the comparative example is high in piercing resistance and further higher after repeated piercing attempts. The quantity of silicone affixed to the flat rubber was increased with the syringe needle referred to in the comparative example. In sharp contrast thereto, the syringe

needle given in the embodiment was low in piercing resistance with no increase in resistance resulting from repeated piercing. The amount of silicone affixed to flat rubber was small. Further, there was no increase in resistance when sterilization was made with ethylene oxide gas or by gamma ray irradiation.

5 [Effect of the invention]

According to the present invention, syringe needles with their resistance to piercing, the resistance not increased by repeated piercing attempts and without limitation to sterilizing means.

10 Claims

1. A syringe needle coated on its outside a mixture of a first polyorganosiloxane resulting from reaction of an alkoxysilane containing epoxy group and both terminal amino groups, and a second non-reactive polyorganosiloxane with the mean degree of polyoxane polyorganosiloxane which the mean degree of polymerization of siloxane part is less than that of the first polyorganosiloxane.
2. A syringe needle according to claim 1, wherein the mean degree of polymerization of siloxane part of polyorganosiloxane resulting from reaction of epoxy group-containing alkoxysilane on both terminal amino groups is 10~10,000.
3. A syringe needle according to claim 1 or 2, wherein the quantity of non-reactive polyorganosiloxane being 1/10~7/10 in weight ratio of polyorganosiloxane caused to react with terminal amino groups.

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